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INVERSION OF SPECTRAL LINESHAPES TO YIELD COLLISIONAL
RATE CONSTANTS

J. Gelfand
Department of Mechanical
& Aerospace Engineering
Princeton University
Princeton, NJ 08544

H. Rabitz
Department of Chemistry
Princeton University
Princeton, NJ 08544

R.B. Miles
Department of Mechanical
& Aerospace Engineering
Princeton University
Princeton, NJ 08544

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Collision Dynamics	Hydrogen Fluoride
Pressure Broadening	Deuterium Fluoride
Rotational Energy Transfer	Laser Photoacoustic Spectroscopy
Hydrogen Chloride	State-to-State Transition Rates

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

State-to-state collisional energy transfer rates are being obtained by the inversion of pressure-broadened linewidth data. Measurements of linewidths in overtone vibration-rotation transitions have yielded information on rotationally elastic and inelastic collision rates for vibrationally excited HCl and HF. Work is continuing in acquiring similar information for vibrationally excited DF, both self relaxation and for relaxation with other collision partners.

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I.   Background and Summary

Collisional interactions between molecules and molecular interactions
with infrared and visible radiation are of essential importance to a large
number of practical phenomena and devices. Much is known about the colli-
sional interactions of molecules in low levels of excitation. However,
because of the experimental difficulties with exciting molecules to higher
levels, little is known about how the mechanisms of molecular interactions
change with increasing vibrational excitation. In particular, very little
is known about molecular interactions at the high levels of excitation
associated with collisions preceding chemical reactions. It is just these
details that are important in practical situations such as high temperature
environments, combusting gases, chemical laser devices and the interaction
of laser energy with matter.

We have been successful in obtaining rotational collisional transfer
rates in the HF system and their change with vibrational excitation of the
colliding molecules [1]. Since the reaction between hydrogen and fluorine
populates a range of rotational levels in high vibrational states, this
system has been of interest as a chemical laser as well as for fundamental
reasons. Vibrational relaxation in HF and DF has been studied by a number
of techniques [2]. However, data on rotational relaxation from the chemi-
cally populated levels is lacking [3]. Modeling has shown that rotational
relaxation is an important parameter in laser operation, particularly affect-
ing output power [4]. In the absence of more sophisticated analysis, current
models tend to include only rotation-translation (R-T) deexcitation [5],
usually characterized by an exponential gap model [5-7]. However, the
results of these studies show an obvious need for a more rigorous determination

of these R-T rates, as well as the importance of including rotation-rotation (R-R) energy transfer rates.

An exact chemical model would require the entire matrix of rotational relaxation rates, a matrix of the order of $10^2 - 10^3$ to include relevant levels. Clearly, the experimental observations of all of these rates is a forbidding and probably impossible task. We have applied the Energy Corrected Sudden (ECS) [8,9] scaling to the inversion of the available self and argon broadened linewidths for HF to obtain the dominant portions of the rate matrix that are consistent with the quantity and quality of experimental data. The determination of any individual collisional transition rate from a single bulk experiment such as pressure broadening has been considered difficult in the past because the pressure broadened linewidth is not very sensitive to any one component rate. In our approach to the inversion of linewidths to yield state to state rates, we are utilizing recently developed scaling relationships which fix the ratios of many rates within a family to a fundamental rate in that class, e.g., rotation-rotation or rotation-translation collisions. A small number of fundamental rates can then be determined by a small number of independent linewidth measurements. Also determined are dynamical factors which allow one to calculate the elastic contributions such as dephasing and the change in the various contributions to the linewidth with the vibrational excitation of the collision partners.

There are two specific advantages to acquiring state-to-state rates by this type of procedure. First, molecular beams or laser fluorescence experiments are amenable to only a limited number of atoms or molecules. Spectroscopic measurements can be done on practically any species. Second, and

most important, experiments that employ state-to-state pumping and subsequent detection of relaxation can only be employed for the lower vibrational levels of only a few molecules which have sufficiently strong overtone absorption cross sections. One can acquire simple absorption spectra for transitions to much higher states than would be feasible for these other techniques. Fortunately in the case of HF and DF, our inversion results can be directly compared with state-to-state pump and probe experiments. Though these are of immediate importance, the simple acquisition of rate data for certain molecules is only one goal of this research program. It is important to obtain specific rates for as many different molecules and collision partners as possible and tie these together to obtain an understanding of the observed trends in terms of the fundamental aspects of collision dynamics.

The specific accomplishments to date on this contract have been:

1) We have acquired overtone absorption data for the HCl-HCl system and have succeeded in learning how to invert the pressure broadened line-width information to obtain state-to-state inelastic rotational collision rates for molecule-molecule systems.

2) We have taken the available literature data for HF-HF pressure broadening and Ar-HF pressure broadening and inverted it to obtain specific rotational relaxation rates.

3) We have carefully studied the problems associated with obtaining spectra to the required level of accuracy needed to study relaxation in the DF-HF system and DF-N_2 system.

4) We have constructed and are now utilizing a laser photoacoustic system to obtain linewidth data for the overtone bands of DF in order to understand the rotational relaxation dynamics of these molecules up to the $v = 6$ state.

II. Progress Report

Using the experience that we have gained in inverting HCl pressure broadening data to obtain inelastic collision rates [9], we have begun our study of the HF system. Collision broadened linewidths were taken from the literature for self-broadening in the fundamental [10] through second overtone bands [11,12] in HF at 100°C and for Argon broadening [13] in the 1-0 and 2-0 bands at 25°C. Results have been obtained for the variation of R-R and R-T rates with vibrational excitation using the ECS scaling theory inversion procedure. We found that rotation-rotation processes are dominant for relaxation in pure HF and that these processes decrease with increasing vibrational excitation of one of the collision partners. We also found that the contribution of rotation-translation mechanisms increases with increasing vibrational excitation for both HF-HF collisions and Ar-HF collisions. Some of the relaxation rates that were extracted in this manner are shown in Figures 1 through 3. Rotation-rotation rate constants for collisions between HF molecules are given in Figure 1. These rates are for collisions in which one molecule is in the ground vibrational state. Curves are shown for collision partners in the ground vibrational state up to molecules in the third vibrationally excited state. The curves are for the particular R-R rates, $k(6j_2 \rightarrow 5j_2+1)$. This rate is for a molecule in $j = 6$ going to $j = 5$ with its collision partner in state j_2 going to state j_2+1. Several notable features can be seen. For ground state molecules the maximum rate is for the collision partners in $j_2 = 5$. This is expected since no energy need be transferred to translation for these resonant collisions. As the level of vibrational excitation increases, the peak in the rate curve shifts to smaller j_2. This is again attributed to energetic effects. Due to the variation in
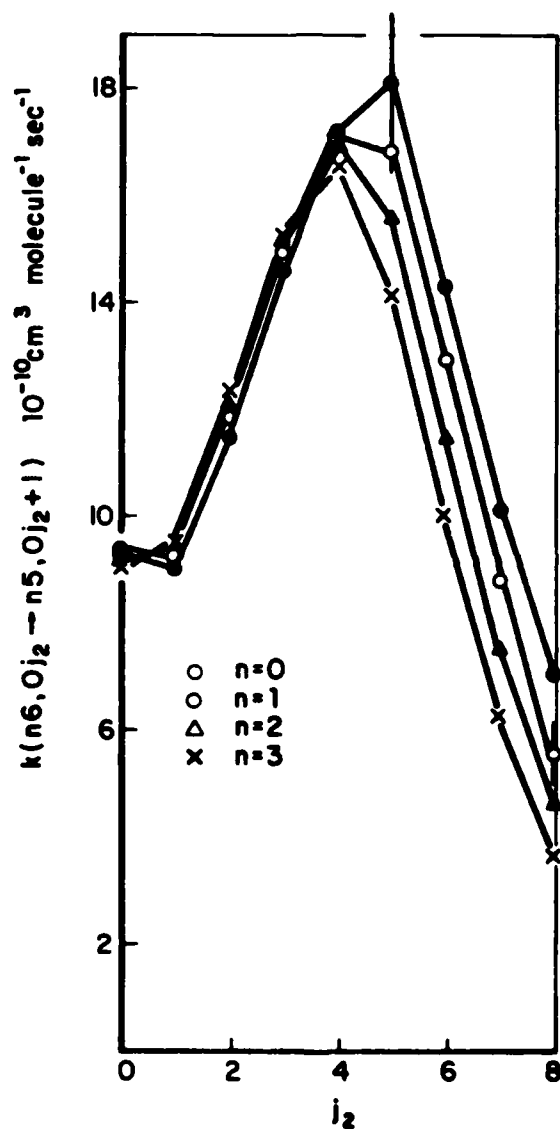
Figure 1. Inverted R-R rates ($j_1 = 6, j_2 \to j_1 = 5, j_2 + 1$) as a function of vibrational level in HF at 100°C. Errors are j-dependent and are calculated via the parameter variation method discussed in the text. The error bars shown here for $n = 0$ and $n = 1$ are intended to impart a sense of the range of the "experimental" errors.

rotational spacing with vibrational level, exactly resonant collisions are not possible with $j_2 = 5$ and those collisions with $j_2 < 5$ are more favorable. In general, off resonant rates are significant and must be included in any modeling attempts of chemical laser performance. The rise in these curves at $j_2 = 0$ is a reflection of "edge effects" that are due to the lack of de-excitation channels for $j_2 = 0$.

Rotation translation rates $k(j_1 \rightarrow j_1 - 1)$, for pure HF and Ar-HF mixtures are shown in Figures 2 and 3, respectively. In the case of self-broadening, R-T rates are less than one half the corresponding R-R rates. The R-T data for Argon broadening at 25°C are approximately an order of magnitude less than those for self-broadening at 100°C. They do, however, exhibit the same qualitative features in that the R-T rates increase with increasing vibrational state of one of the collision partners. This behavior can again be related to the change in rotational spacing with vibrational level. The rotational constant and hence the difference in adjacent energy levels, decreases with higher n. Consequently, less energy must be transferred to translation and the process is more favorable.

Multi-quanta transition rates are more difficult to extract than single quanta rates for two reasons. Additional fundamental rates and dynamical factors are needed which require more data of a higher precision for a meaningful extraction of these parameters in the inversion procedure. More precise data is also required because these higher order processes constitute a much smaller percentage contribution to the linewidth than the single quanta dipole coupled processes. We did not attempt to extract the multi-quanta R-R transition rates from the pure HF pressure broadening. We would expect the near resonance $\Delta j = 2$ R-R collisions would be the larger contributor
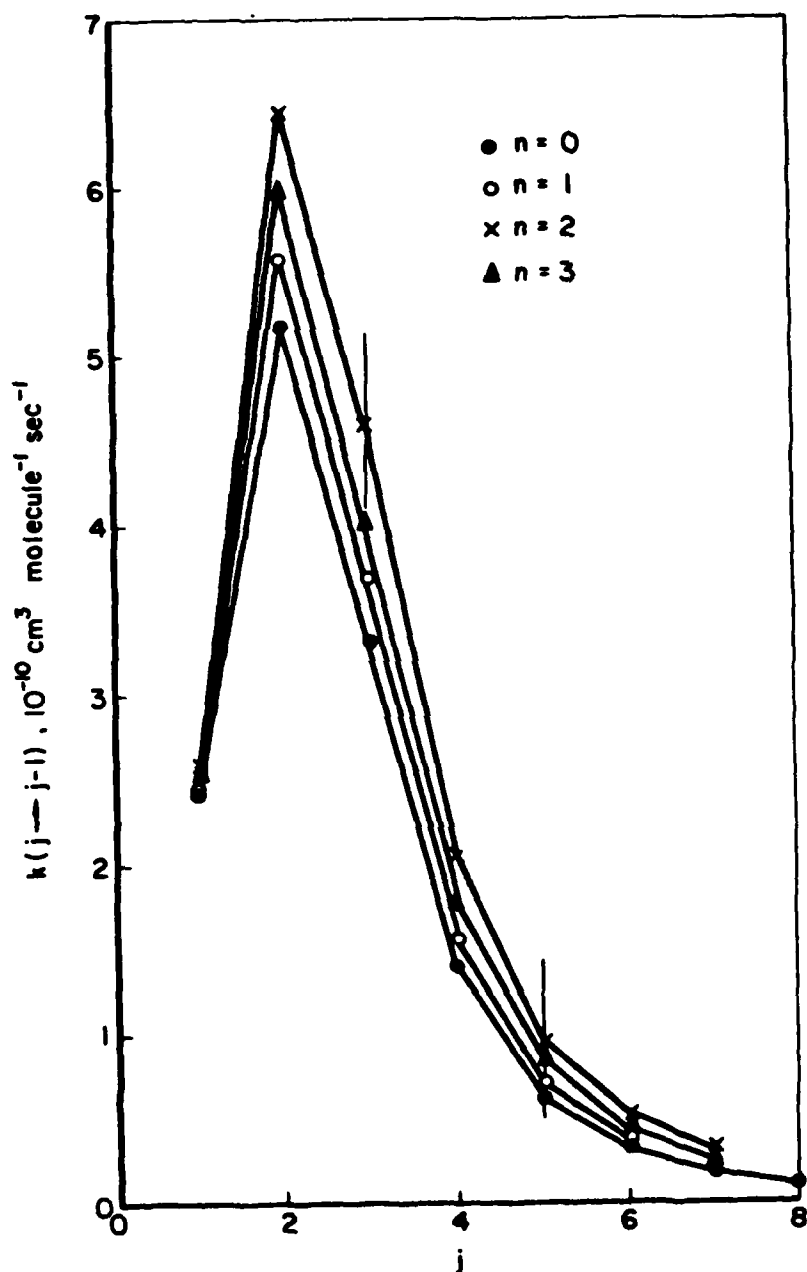
Figure 2. Inverted ($\Delta j = -1$) R-T relaxation rates as a function of vibrational level in pure HF at $100°C$. Errors are j-dependent and are calculated via the parameter variation method discussed in the text. The error bars shown here for $n = 0$ are intended to impart a sense of the range of the "experimental" errors.
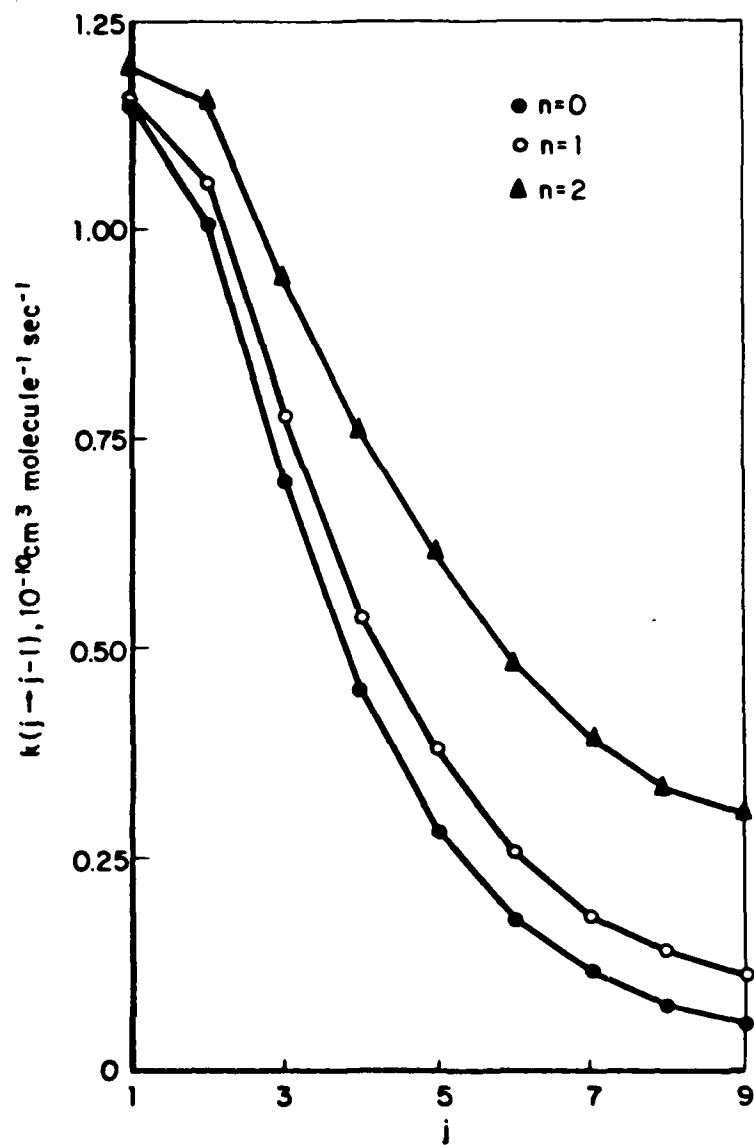
Figure 3. Inverted ($\Delta j = -1$) R-T relaxation rates for various vibrational levels in Ar-HF mixtures at 25°C.

to this class. Using the ECS scaling relations we have synthesized the contributions of these processes to the linewidth and have concluded that the precision of the available experimental data precludes a determination of the fundamental rates for these processes. Our analysis indicated that the $\Delta j = 1$ R-R rates extracted from the linewidths may be somewhat larger to compensate for neglecting the higher order collisional transitions. The upper limit on the error introduced in the R-R rates because of this is estimated to be 15%. However, this will have no effect on the trends given here. We feel that an experimental accuracy in the range of 1-2% is required to obtain some of the more significant higher order transitions.

These results are in substantial disagreement with the theoretically calculated rates of Wilkins at Aerospace Corporation [14]. The latter calculations are both quantitatively in disagreement and show physically incorrect behavior. Our own relaxation rates are in much closer agreement with the independent experimental measurements made by Hinchen [15] at United Technologies and Crim at Wisconsin [16].

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III. Publications During the Term of This Contract

1. M. Zughul, J. Gelfand, H. Rabitz and A. DePristo, "Pressure Broadening in the 0-4 through 0-7 Overtone Bands of $H^{35}Cl$ and $H^{37}Cl$", JQSRT $\underline{24}$, 371 (1980).

2. R. Miles, J. Gelfand and E. Wilczek, "Thin Filament Interferometric Microphone", J. Appl. Phys. $\underline{51}$, 4543 (1980).

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4. E. Wilczek, J. BelBruno and J. Gelfand, "Voigt Profiles of Spectral Lines: Accuracy of Line Parameters as a Function of Peak Transmittance", Applied Spectroscopy, in press (1981).

5. J. BelBruno, M. Zughul, J. Gelfand and H.Rabitz, "Analysis of Collision-Broadened and Overlapping Spectral Lines to Obtain Individual Line Parameters", J. Mol. Spec., in press (1981).

6. J. Gelfand, M. Zughul, H. Rabitz and C.J. Han, "Line Strengths in the 0-4 through 0-7 Overtone Bands of HCl", JQSRT, in press (1981).

7. S. Augustin, J. BelBruno, H. Rabitz and J. Gelfand, "A Rapidly Convergent Expansion Technique for Local Quantum Mechanical Operators", J. Chem. Phys. submitted (1981).

8. J. BelBruno, J. Gelfand and H. Rabitz, "Rotational Relaxation Rates in HF and Ar-HF from Direct Inversion of Pressure Broadened Linewidths", J. Chem. Phys. in press (1981).

IV. Graduate Students and Postdoctoral Personnel Associated with this Contract

Ms. Elizabeth Wilczek, Masters Degree, 1981.

Dr. Joseph J. BelBruno, Postdoctoral Research Associate.

V. Current Support

Title	Supporting Agency	Dates	Award Amount	Man-Months or % of Effort Committed
I. Gelfand, Miles, Rabitz - Joint Contracts				
Experimental and Theoretical Study of Relaxation from Highly Vibrationally Excited Hydrogenic Molecules	NSF	8-1-78 36 mo.	$219,000	Gelfand 18 mo. Miles 3 mo. Rabitz 3 mo. (summer)
Inversion of Spectral Line Shapes to Yield Collisional Rate Constants	ONR	9-1-80 13 mo.	69,057	Gelfand 3 mo.
II. Gelfand, Royce, Benziger - Joint Contracts				
Fourier Transform Spectrometer for Materials Research	NSF	6-1-81 12 mo.	80,000	
III. H. Rabitz				
Collisional Studies of Gaseous Molecular Lasers	ONR	5-31-81 12 mo.	75,000	2/3 summer
Dynamical Studies of Molecular Systems (with A. Askar, A. Cakmak)	DOE	2-1-81	70,000	
Finite Element Method for Atom-Molecule Reactive Scattering	NSF	9-1-80 12 mo.	45,000	1/6 summer
(with S. Augustin) Non-Equilibrium Statistical Mechanics	AFOSR	10-1-80 12 mo.	63,655	
Studies of Energetic Material Dynamics	ONR	7-1-80 12 mo.	45,869	1/6 summer
IV. R.B. Miles				
Picosecond Nonlinear Raman Spectroscopy of Surfaces	NSF	11-30-80 12 mo.	58,157	summer
Turbulence Measurements in High Speed Flows by Resonance Fluorescence	NASA/Ames	1-1-79 24 mo.	89,239	1 mo. academic year
V. R.B. Miles, L. Sweet - Joint Contract				
Aircraft Position Measurement Using Laser Beacon Systems	NASA	6-1-81 18 mo.	174,000	1 mo. academic year